USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 311
ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AIR AND SOIL VAPOR

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1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the analysis of volatile organic compounds (VOCs) in air and soil gas samples collected in specially prepared stainless steel canisters or Tedlar bags. This SOP is based on EPA Method TO-15, Second Edition, January 1999. Deviations from Method TO-15 are described in Appendix A. Analytes and quantitation limits (QLs) are listed in Appendix B.

This SOP is applicable to the analysis of VOCs greater than the concentrations listed in Appendix B in air and soil vapor; refer to USEPA Region 9 Laboratory SOP 314 *Low Level Analysis of Volatile Organic Compounds in Air by GC/MS Selected Ion Monitoring* for the analysis of lower concentration air samples.

2 METHOD SUMMARY

A known volume of sample is directed from the sample container through a sample loop or mass flow controller to a micro-scale purge and trap, separated in the GC column, and detected by a mass spectrometer (MS). Standards are analyzed under the same conditions as employed for samples. The target VOCs are identified in the sample by comparing the sample mass spectra to mass spectra in the National Institute of Standards and Technology (NIST) Library and comparing sample GC retention times to the analyte retention times in the standards. Each target compound is quantitated using relative response factors from the most recent initial calibration.

Non-target compounds, when requested, are identified by comparing the resulting mass spectra of the non-target compound to the mass spectra contained in the National Institute of Standards and Technology (NIST) Library in the MS database. An estimated quantitation is performed for the non-target compounds by comparing the total MS response to the nearest internal standard total MS response, assuming a relative response factor of 1.0.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

FC43: Perfluorotributylamine. Compound used to tune the MS.

GC/MS Tuning Solution (MS tune): Bromofluorobenzene (BFB) used to evaluate the performance of the GC/MS system with respect to a defined set of method criteria.

sccm - Standard Cubic Centimeters per Minute (mL/min).

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4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the EPA Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: vinyl chloride and trichloroethylene. Primary standards of these toxic compounds are prepared from commercially prepared gas reference standards that are available in various gas cylinder sizes. These standards must be prepared in a hood. If standard preparation is by dynamic dilution of the gaseous contents of a cylinder of stock gas calibration standards, then the dilution system must be vented into a hood.

The procedure described in this SOP uses cryogenic liquids for cooling the Entech concentrator. USEPA Region 9 Laboratory SOP 770, *Handling Cryogenic Materials*, provides guidelines for the safe handling of cryogenic materials.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

All compressed gas cylinders must be securely chained to laboratory benches or walls and placed so that the label can be easily read.

Canisters must never be pressurized beyond 40 psig, which is the maximum allowable pressure for specially prepared canisters.

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4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

No solvents are utilized in this method except the very small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials in preparing standards and sample preservatives. All are used in very small amounts and pose no threat to the environment.

4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The Laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with USEPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure*. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, standards cylinders* etc.)	Non-hazardous Waste	Not applicable
Methanol waste (methanol, halogenated volatile compounds)	Hazardous Waste	Flammable, toxic
Waste pump oil (trace halogenated volatile compounds)	Hazardous Waste	Toxic

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Waste Stream Description	Waste Label	Hazard Properties
Spent stock standard cylinders (depleted or expired): vent to ambient pressure in fume hood prior to disposal	Recycled / Non-hazardous Waste	Not applicable

*Used cylinders are returned to the manufacturer or punctured, vented, and treated as non-regulated waste.

Stock standard cylinders purchased from Restek Corporation (Spectra Gases, Inc.), when ready for disposal, are vented in a fume hood to < 15 psig, labeled "EMPTY", and are returned to the manufacturer: Environmental Division, Spectra Gases Inc., 80 Industrial Drive, Alpha NJ, 08865.

Stock standard cylinders purchased from Supelco (Sigma-Aldrich), when ready for disposal, are vented in a fume hood to ambient pressure, labeled empty, made unusable by drilling a hole through the cylinder, and disposed of with the non-regulated waste.

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples should be collected in specially prepared stainless steel canisters (hereafter referred to as SUMMA canisters) or Tedlar bags. Canisters included are SUMMA7 polished interior canisters, SilcoSteel silica coated interior canisters, TO-Can electro-polished interior canisters, and Silonite coated interior canisters. Canister sizes vary from 400-mL to 6-L.

5.2 Internal Chain-of-Custody

After samples are received and logged into the Laboratory Information Management System (LIMS), they are delivered by the Sample Custodian to Room 203. If active samples are moved from Rooms 201/203, update the LIMS internal custody form.

Verify sample IDs and dates and times of collection against the chain-of-custody form. If discrepancies are noted, inform the sample custodian.

Check the following information to ensure that the information on the sample containers corresponds to the information on the tracking sheets and the chain-of-custody record.

- ☐ EPA work order number
- ☐ Laboratory ID number

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- Case number
- Sample delivery group number

Sample canisters should have pressures below ambient upon receipt if passive flow controllers were used. Confirm that the integrity of the sample has not been compromised by checking canister pressure. During sample pressurization, compare the initial pressure reading to the pressure recorded on the COC in the field. Note any significant difference (more than 10%) in the LIMS work order memo field and request guidance from the supervisor or Technical Director.

5.3 Preservation Verification and Storage

Samples should be received and stored at ambient temperature.

5.4 Holding Time

Samples in SUMMA canisters shall be analyzed within 30 days of sampling. Samples in Tedlar bags shall be transferred to SUMMA canisters or analyzed within 72 hours of the time of sampling.

Sort samples according holding times (see above paragraph) and analyze to prevent exceeding the holding time. Review due dates and project notes to prioritize RUSH samples (while meeting all sample holding times).

Excess air or soil gas sample in canisters and Tedlar bags should be stored in the storage racks in the air analysis laboratory. Upon completion of the analysis for an SDG, the excess samples for the entire SDG should be stored, for a minimum period of seven days after the submission of the data deliverables associated with the sample delivery group (SDG). After seven days, canisters should be cleaned as specified in USEPA Region 9 Laboratory SOP 312, *Cleaning and Certification of Specially Prepared Canisters for Soil gas Sampling*. After seven days, the Tedlar bags shall be opened in the fume hood. If this requirement jeopardizes the supply of clean canisters to field samplers the Chemistry Technical Director must be notified and permission to clean canisters prior to the 7-day courtesy hold requested.

6 INTERFERENCES

Interferences in canister samples may result from contamination of canisters due to poor manufacturing practices. To minimize this possibility, new canisters should be cleaned and certified as specified in SOP 312 prior to use. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components.

Contamination may occur if canisters are not properly cleaned. Before each use, canisters must be thoroughly cleaned and certified as outlined in SOP 312.

Canisters should be capped tightly during storage and shipping to prevent leakage and minimize any compromise of the sample.

Interferences in Tedlar bag samples may result from contamination of bags due to poor manufacturing practices or improper handling. To minimize this possibility, the laboratory encourages samplers to flush Tedlar bags at least three times with high purity nitrogen (99.998%) prior to use.

Impurities in the calibration dilution gas and carrier gas, organic compounds out-gassing from system components ahead of the trap, and solvent vapors in the laboratory account for the majority of laboratory contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. Zero air should be humidified with organic free water that has been prepared according to USEPA Region 9 Laboratory SOP 205, *Preparation of Organic-Free Method Blank Water*. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with rubber components must be avoided.

Significant contamination of the analytical system can occur whenever samples containing high VOC concentrations are analyzed. Whenever an unusually concentrated sample is analyzed, it should be followed by analysis of an instrument blank to check for carry-over contamination.

High carbon dioxide levels may interfere with early eluting compounds.

High methanol levels (more than 0.5 uL per injection) may degrade chromatographic performance, cause tailing, and/or erratic response.

Water may degrade chromatographic performance. The system is designed to handle moisture levels typically encountered in ambient air. Samples which contain high concentrations of water vapor may require special handling. Consult with the Chemistry Technical Director to determine the appropriate analysis steps.

Solvents and other compounds that are target analytes must never be introduced into the laboratory where volatiles analysis is performed. Dichloromethane and other common laboratory chemicals are target analytes under this SOP and must be excluded from Rooms 201 and 203. Particular attention must be paid to the possibility of transport of solvent vapors on individuals. Analysts should never enter Rooms 201 or 203 after being in the extraction laboratories or glassware washing area.

Contamination from field samples can build up in the manifold system. The manufacturer recommends flushing the system using the flush routine at the start of every week when the system is actively utilized. Refer to the system manual for additional details.

Cross contamination on the ambient autosampler has been observed when the attached canister pressures vary significantly. It is therefore recommended that the can pressures be

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kept in the 7-30 psia range. It is also recommended that the canister be removed from the sampler as soon as the analysis is completed.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

- GC/MS System

  Gas Chromatograph (GC): Hewlett Packard/Agilent 6890 or 6890N, or equivalent. The GC must be capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with an automatic sample injector, split/splitless injection port, and electronic pressure control (EPC).

  Column: RTX624, 60 m length, 0.32 mm ID, 1.8 micron film capillary column, (Restek catalog # 10972) or equivalent. Any column capable of separating the target analytes and passing method QC without overloading at the concentration of the highest standard may be used.

  Mass spectrometer: Hewlett Packard/Agilent 5973 or 5973N, or equivalent, capable of scanning from 35 to 500 amu every one second or less using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be able to produce a mass spectrum that meets acceptance criteria when 50 ng or less of BFB is introduced onto the GC system.

- Data system: ChemStation (available from Agilent), or equivalent, able to control the GC/MS system and to acquire, store, and reduce mass spectral data. The software must be able to process any GC/MS data file by recognizing a GC peak within a retention time window, comparing the mass spectrum from the GC peak with spectral data in a database, and generate a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time and scan number limits and to calculate RRFs and concentrations of analytes in samples.

- Cryogenic Concentrator: Entech 7100A pre-concentrator, or equivalent.

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- Autosampler: Entech 7032-L Ambient canister autosampler, or equivalent.

- Autosampler: Entech 7032A-L Loop canister autosampler, or equivalent.

- SUMMA Canisters: Polished canister with SilcoSteel coated interior, Entech part number 29-MC1000S (1 L) and Entech part number 01-10622 (6 L) size or equivalent.

- MiniCan: 400 mL SUMMA canister equipped with quick-connect fittings and Silonite lining, Entech part number 29-MC400S or equivalent. The can should also be equipped with a MiniCan Cap to protect the quick connect valve during shipping, Entech part number 29-CAP-CH or equivalent.

- Entech 4600 dynamic diluter: This system is used to create calibration standards by diluting stock standards. It is also used in diluting samples. The diluter uses Mass Flow Controllers to perform the dilutions.

- Entech 3100A Canister Cleaner and associated equipment.

Other GC/MS, concentrator, or autosampler systems with similar configurations can be used to analyze samples following this SOP as long as the instrumentation produces data that meets the QC criteria of this SOP.

7.2 Reagents

The following reagents are to be used at the specified or higher grade:

- Helium gas — (Ultra High Purity)
- Liquid nitrogen (50 psig and 350 psig)
- Nitrogen gas
- Air, Zero Grade (e.g. Praxair Part # AI 0.0Z)
- Organic-free water (EPA Region 9 Laboratory SOP 205 *Preparation of Organic-free Method Blank Water*)

7.3 Standards

When ordering standards from various suppliers it is important to determine that the primary and secondary sources are truly independent. Experience has shown that suppliers frequently purchase gas phase standards from outside sources. For example, supplier A may ship lot #1; supplier B ships lot #34, but both suppliers purchased the cylinders from supplier C who only prepared one lot.

All stock standards upon receipt must be recorded into the LIMS and assigned a standard ID number. Sources, expiration dates, components, and concentrations for gas

mixtures must be recorded onto the LIMS. Standard ID number and expiration dates must be printed on to the standard cylinder's label. Store all standards at room temperature.

Working standards should be allowed to equilibrate for at least 2 hours after preparation prior to use. Store air standards at room temperature.

Stock Standards - Stock standard solutions may be purchased as certified mixtures or prepared from ACS reagent grade materials.

- Internal Standard Gas Mixture - commercially prepared certified custom gas mixture containing the following with nitrogen making up the balance: bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene. Restek/Spectra Gases TO-14A mix, catalog no. 34427 (100 ppbv), catalog no. 34412 (1 ppmv), or equivalent.

- 4-Bromofluorobenzene Tuning Standard - commercially prepared certified gas standard containing nominally 100 ppbv of BFB that is equivalent to 0.78 ng BFB per mL of standard mix. Restek catalog no. 34424 (100 ppbv), Restek catalog no. 34406 (1 ppmv), or equivalent.

$$\frac{175\,g_{BFB}}{mole_{BFB}} \times \frac{100 \times 10^{-9}\,moles_{BFB}}{mole_{Nitrogen}} \times \frac{1 \times 10^{9}\,ng_{BFB}}{g_{BFB}} \times \frac{mole_{nitrogen}}{24{,}470\,mL_{Nitrogen}} = 0.715\,ng_{BFB}/mL$$

- Calibration Gas Standard (stock) Primary list- commercially prepared certified gas standards containing target compounds. Restek/Spectra Gases TO-14A Calibration Mix, 1ppm in nitrogen, catalog no. 34400; Restek/Spectra Gases TO-14A Calibration Mix, 100 ppbv in nitrogen, catalog no. 34421;

- Calibration Gas Standard (stock) Subset list- commercially prepared certified gas standards containing target compounds. Restek/Spectra Gases TO-15 Subset 25 Component Mix, 1ppm in nitrogen, catalog no. 34434; Restek/Spectra Gases Subset 25 Component Mix, 100 ppbv in nitrogen, catalog no. 34435, or equivalent.

- Second Source Verification (stock) Primary list- commercially prepared certified custom gas standard containing target compound derived from a secondary source. Supelco EPA TO-14 Calibration Mix 1 in nitrogen, catalog no. 41900-U (100 ppbv); or Supelco EPA TO-14 Calibration Mix 1, catalog no 509981 (1 ppmv), or equivalent.

- Second Source Verification (stock) Subset list- commercially prepared certified custom gas standard containing target compound derived from a secondary source or different standard lot depending on commercial availability.

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7.3.1 Preparation of Calibration Standards

Working calibration gas standards are prepared by diluting commercially prepared certified gas standards. Calibration standards at various concentrations are derived by varying the volumes loaded during the pre-concentration step.

7.3.2 Preparation of Working Calibration Standards

The working calibration standards are prepared in SilcoSteel silica coated canisters using the Entech 4600 dynamic dilution system to a final canister pressure of 30 - 40 psia. The Entech 4600 uses mass flow controllers and humidified ultra high purity zero grade air to dilute stock standards to the desired concentration used for calibration.

The concentration of the working standard is calculated using the following equation:

$$C_F = C_I (f_i / f_t) = C_I (f_i / f_d + f_s) \text{ since } f_t = f_d + f_s$$

Where:

C_F is the final concentration of the working standard
C_I is the initial concentration of the calibration standard
f_i is the flow rate from the calibration standard
f_d is the flow rate of the dilution gas (humidified zero air)
f_s is the sum of all flow rates
f_t is the total flow rate

To prevent cross-contamination, the front diluter is reserved for sample pressurization and to prepare standards from 100 ppbv parents. The back diluter is used to prepare more concentrated standards.

To prepare working standards from two 1 ppmv standards (primary and a subset), the following are typical diluter flow rates:

C_F	Zero air flow (sccm)	1 ppmv Standard flow (sccm)
20 ppbv	2400	50 Primary 50 Subset
10 ppbv	2450	25 Primary 25 Subset

To prepare working standards from a single 100 ppbv standard, the following are typical diluter flow rates:

C_F	Zero air flow (sccm)	100 ppbv Standard flow (sccm)
20 ppbv	1600	400

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C_F	Zero air flow (sccm)	100 ppbv Standard flow (sccm)
10 ppbv	1800	200

To prepare working standards from a 100 ppbv and 1 ppmv standards, the standard is prepared in two steps; the following are typical diluter flow rates:

Step #1: an evacuated can is attached to diluter #1 (typically the front diluter).

C_{F*}	Zero air flow (sccm)	100 ppbv Standard flow (sccm)
20 ppbv	600	400
The standard is collected until a final pressure of 20 psi is reached		

*See note.

Step #2: The can is moved to the back diluter and the following standard is introduced

C_{F*}	Zero air flow (sccm)	1 ppmv Standard flow (sccm)
20 ppbv	2400	100
The standard is collected until a final pressure of 40 psi is reached		

*See note.

Note: When two standards are added to the same can, the concentrations are calculated using the total final volume. The final concentrations listed in the tables refer to the concentration after both standards are added to the can.

7.3.3 In-House Prepared Calibration Standards –

Standards may be prepared in-house using the procedure outlined in Appendix E.

Replace working calibration standards every 30 days, when the canister pressure is below ambient (i.e., 10 psia or -5 psig), or sooner if analysis indicates that the standard has degraded.

7.4 Supplies

- Stainless steel tubing and stainless steel fittings.
- Stainless steel cylinder pressure regulator - standard two-stage cylinder regulators with pressure gauges (low pressure side should have a range of $\leq$ 100 psi).
- Pressure gauge with stainless steel wetted parts with +0.25% accuracy.
- Vacuum gauge with Monel process connection with +0.25% accuracy.
- Gas-tight syringes (1-mL, 5-mL, 25-mL and 50-mL).

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Check the mass spectrometer for leaks on a daily basis, prior to the analysis of the tuning compound using the instructions provided in Appendix D. Generate and print a leak check report and include in the data package.

Samples may be introduced using the loop mode or ambient mode. Set up the Entech autosampler parameters according to parameters in Appendix D.

Set-up the GC/MS following operating instructions provided by the manufacturer. Use operating parameters provided in Appendix D as a starting point.

8.1.1 GC/MS tuning:

Mass calibration of the analytical system must be performed prior to an initial calibration, whenever the source is cleaned, or whenever a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions. Use perfluorotributylamine (FC43) to perform mass calibration of the instrument.

Calibrate the Mass Axis of the MS prior to analyzing the BFB standard. Use the settings in the most recent tune file as the initial conditions; save the tune file using the naming convention in Appendix E, and generate a tune report.

Refer to Section 9 and Appendix C for acceptance criteria and corrective action requirements.

8.1.2 GC/MS System Performance Check (BFB analysis)

The GC/MS system must meet the mass spectral ion abundance criteria for BFB prior to analysis. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target compounds.

Introduce approximately 30 ng of BFB onto the analytical system using the operating parameters provided in Appendix D.

The autofind procedure will automatically find the BFB peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex), perform a background subtraction, and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances.

Refer to Section 9.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

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Save the method as outlined in the "ChemStation File Naming Convention" (see Appendix F) using today's date "mmdd" in the file name under D:\MSDCHEM\Year\Methods\.

8.2 Calibration and Standardization

8.1.3 Initial Calibration

Refer to Section 8.4 for system maintenance procedures that may be required prior to analyzing an initial calibration.

Perform auto-tune or manual tune, and introduce the BFB tuning standard.

Perform an initial calibration using six calibration levels. Refer to Section 9 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Calibration levels 1, 2, and 3 are analyzed using the ambient mode. Calibration levels 4, 5, and 6 may be analyzed using either the ambient mode or the loop mode. Note that the loop and ambient modes produce equivalent results. The calibration may be performed using only the ambient mode even if samples are subsequently analyzed on the loop.

The recommended concentrations for ambient and loop modes are listed in the following tables. Note that in the loop mode the amount of sample introduced to the instrument is determined by the loop size and by the split ratio. For a 1 mL loop without splitting, the sample introduced is 1/200 of the ambient mode.

Calibration Standards, Ambient Mode

Calibration Level	Concentration, ppbv	Internal Gas Standard Mix, 100 ppbv, mL	Working Calibration Standard	Volume, mL
1	20	40	20 ppbv	200
2	15	40	20 ppbv	150
3[1]	10	40	20 ppbv or 10 ppbv	100 of 20ppbv or 200 of 10 ppbv
4	5	40	10 ppbv	100
5	2	40	10 ppbv	40
6[2]	1	40	10 ppbv	20

[1]CCV or LCS may be analyzed at level 3 or 4
[2]QLS

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Calibration Standards, Loop Mode (1 mL Loop)

Calibration Level	Concentration, ppbv	Internal Gas Standard Mix, 100 ppbv, mL	Calibration Gas Standard	Split[1]
4[2]	5	40	1,000 ppbv	0
5	2	40	1,000 ppbv	2.5
6[3]	1	40	1,000 ppbv	5

[1]Split is achieved by varying sample/split vent flows; see Appendix D.
[2]CCV or LCS may be analyzed in the loop mode, particularly if all samples use the loop.
[3] QLS

Check the initial calibration for misidentified peaks due to retention time shifts. The most commonly misassigned compounds are 1,3- and 1,4-dichlorobenzenes.

No quantitation ion may saturate the detector.

The data system calculates the relative response factor (RRF) for each target compound for all calibration standards using the following equation. The quantitation ions and internal standard assignments are listed in Appendix C.

$$RRF = (A_x)(C_{is})/(A_{is})(C_x)$$

Where

A_x = Area of quantitation ion of compound x
A_{is} = Area of quantitation ion for associated internal standard
C_x = Concentration of compound x
C_{is} = Concentration of the associated internal standard

Check and print the calibration by performing the following steps:

1. In the ChemStation data analysis module, load the current initial calibration method from D:\MSDCHEM\Year\Methods\
2. Perform an initial calibration using the recommended concentrations listed in Section 8.2.1.
3. Update the response factors in the method using the newly acquired calibration files.
4. Update the retention time in the method using the newly acquired continuing calibration level.
5. Update the qualifier ion relative responses from the CCV calibration level.
6. Save the method as outlined in the "ChemStation File Naming Convention" (see Appendix F).
7. Generate "Response Factor Report."
8. Check the calibration files listed on the "Response Factor Report" to insure that the correct files are being used.

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9. Check the time and date to ensure that the correct update is used.
10. Process the SCV with the newly created initial calibration, check to make sure the "QLast Update" time and date match the "Response Factor Report"
11. Open and immediately close Chemstation Custom Reports. (Note: no Chemstation custom reports are actually used, opening and closing custom reports populates "detail.xls" which is later mined for data.)
12. Open the latest copy of C:\msdchem\custrpt\ "Full_Custom_Report.xls" Make sure automatic updates of links is enabled under options.
13. Go to the "SCV Recovery","ICAL Area", "ICALconc", tabs and print reports. Make sure the SCV passes acceptance criteria (Appendix C) and the ICAL areas match what is on the Chemstation quant reports.
14. Verify that the method was updated correctly. Print the Compound List Report from ChemStation. Verify that the average response factor is used. Scrupulously check the elution order and retention times, compare them to an old ICAL if needed.
15. Copy the method to I:\RoomNumber\Instrument\Year\Methods\
16. Manually calculate a result for one surrogate in the SCV to insure that the correct RFs are being used and write the results on the quantitation report.
17. Save a hard copy of the initial calibration files so they may be copied and included in associated packages.

The analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are not contaminated. This is accomplished through the analysis of a method blank or an instrument blank.

Refer to Section 9 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Calibration note: on occasion, an analytical system calibrated for a specific project must be used to analyze samples requiring additional compounds. Additional calibration standards may be analyzed and added to the method. The method update must be thoroughly documented. Note that the internal standards in the method will be those acquired during the first analyses and the RRFs for the additional compounds will use the earlier internal standard area count. Therefore, it is important that the internal standards of the added calibration points demonstrate similar response to prevent significant error in the RRFs used for quantitation.

8.1.4 Continuing Calibration Verification

Analyze a calibration verification standard by performing the following steps:

1. In the ChemStation data analysis module, load today's method from D:\MSDCHEM\Year\Methods.
2. Acquire the continuing calibration using today's method.

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3. Quantitate the continuing calibration file.
4. Generate "Evaluate Continuing Calibration Report".
5. Compare the IS retention times and areas in the CCV standard to the mid-point standard of the most recent initial calibration. Adjust the electron multiplier (EM) voltage if needed (an increase of 50 volts will typically double the response). If the EM voltage is changed, reanalyze BFB and the CCV.
6. Manually calculate the result for one surrogate to insure that the correct RFs are being used. Record the result on the quantitation report.
7. As each run is quantitated during the day, make sure that the same date and time stamp, (e.g. "QLast Update : Mon Jul 25 08:15:58 2011"), is recorded on each file header.
8. If QLast Update time stamp changes, state the reason, repeat steps4 through 7 above, and include the reports generated in the package.
9. Save a copy of the method to the LAN, when the data are backed up to the LAN the following day.

Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.1.5 Quantitation Limit Verification Standard (QLS)

Analyze a quantitation limit standard at the concentration of the lowest point of the initial calibration.

The QLS must be analyzed on the loop if samples are to be reported from the loop.

Use the full_custom_report to calculate the QLS recoveries.

Refer to Section 9.2.4 and Appendix C for acceptance criteria and corrective action requirements.

8.3 Analysis

Sample canister pressures are checked and recorded by the analyst upon receipt in room 203 using the Entech 4600 dynamic diluter. Canisters are typically pressurized to a 1.5x dilution in order to bring canister pressures above ambient (approximately 15 - 25psia). Dilution procedures and calculations are recorded in the Dilution Logbook. Record canister number, initial canister pressure, final canister pressure, and the ambient pressure readings in the dilution logbook. An example of the Dilution Logbook is provided in Appendix G.

8.3.1 Sample Preparation

Check that the serial numbers on the canisters coincide with the numbers on the routing forms to ensure that the correct sample is being analyzed.

Samples in Tedlar bags can only be analyzed using the ambient mode unless the sample is transferred to a SUMMA can.

Check the canister pressure and record the initial canister pressure, final canister pressure, and the ambient pressure readings in the Dilution Logbook even if sample dilution is not necessary. An example of the Dilution Logbook is provided in Appendix G.

If sample canisters are < 10 psia, pressurize canister to a recommended pressure of 15-25 psia.

If sample pressure is >10 psia, it may be analyzed without dilution in the ambient mode; therefore, the sample need not be pressurized. Record the initial pressure reading in the dilution log regardless if dilution is performed or not.

Samples scheduled for loop mode analysis must be pressurized to a recommended pressure of 15-25 psia.

The presence of liquid water in samples received in minicans (400 mL or 1L) has been known to cause catastrophic concentrator failure. If the presence of water is suspected, screen the field sample by placing a paper towel on a flat surface and releasing 1-2 mL of the sample on the towel by momentarily pressing the pressurized canister valve against the towel. If water is noted on the towel, contact your supervisor or the Chemistry Technical Director prior to analyzing the sample.

Analysis of 200 mL sample load volume represents an undiluted sample (i.e. Dilution Factor = 1). If samples are expected to be highly contaminated or are of unknown concentration, screen the samples in the loop mode to 1) protect the analytical system from damage or contamination and 2) to determine the appropriate subsequent dilutions. If the sample history is known, select the appropriate dilution, mode, and split ratio to stay within the instrument calibration range.

8.3.2 Sample Dilution

If the on-column concentration of any target compound in any sample exceeds the initial calibration range, a dilution of the sample should be analyzed. Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

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When possible, choose a dilution factor that keeps the response of the largest target compound in the upper half of the initial calibration range of the instrument.

Dilution of the sample can be accomplished by reducing the sample volume taken during the pre-concentration step; however, a sample volume lower than 10 mL is not recommended using the ambient autosampler. Enter the sample volume utilized in the "initial sample volume" column of the LIMS bench sheet. Final Volume is 200 mL which is the default sample size.

Dilution may also be accomplished by re-pressurizing sample canisters. For re-pressurized canisters, the sample dilution factor is calculated as follow:

DF = Pf/Pi where
DF: Dilution Factor
Pf: Final canister pressure
Pi: Initial canister pressure

If further dilution is necessary, an aliquot of the original sample should be taken and diluted into a certified clean canister with zero air. Pressurize the certified canister to 10-15 psia. Draw a known volume aliquot from the sample canister and inject the aliquot in the dilution can. Measure the final can pressure and record the reading in the "final" pressure column of the Dilution Logbook. For samples diluted in secondary canisters, the dilution factor is calculated as follow:

DF = (Pf*Vi)/(Pi*Vf) where
DF: Dilution Factor
Pf: Final canister pressure
Vi: Volume of aliquot
Pi: Ambient pressure
Vf: Final volume (i.e. 400 mL for 400 mL cans)

Record canister number, initial canister pressure, final canister pressure, and the ambient pressure readings in the Dilution Logbook.

The diluted sample should be allowed to equilibrate for 2 hours after preparation before analysis. This is particularly important when dilutions are performed to quantitated heavy compounds (i.e. target analytes that elute after the last internal standard).

In the case of extremely contaminated samples, several dilutions and volume variations may be required.

8.3.3 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument run log and the LIMS sequence page.

Load the samples in the autosampler according to their designated positions in the sequence file. The following steps represent the recommended analysis sequence:

1. BFB/Primer
2. CCV/LCS
3. CRL (QLS)
4. MB
5. Samples
6. Sample dilutions, as needed
7. Instrument Blanks, as needed

Enter sample sequence in the instrument software. Include the Laboratory ID (WO-sample number) in the "Sample" field and dilution level, if any, in the "Multiplier" field.

Name the data files according to the data file naming convention outlined in Appendix F.

8.3.4 Instrument Blanks

In the event that a sample is analyzed which exceeds the calibration range of the instrument, an instrument blank should be analyzed to demonstrate that the system is free of carryover contamination.

At a minimum, the analyst must evaluate the next sample to determine if carryover may have occurred by either:

- Analyze an instrument blank immediately after the contaminated sample.
- Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample that exceeded the limits above.

The instrument blank is acceptable if it meets criteria listed in Appendix C.

Instrument blanks may be analyzed beyond the 24-hour tune time period.

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8.3.5 Analyte Identification and Quantitation

8.1.5.1 Analyte Identification

In order for a target compound to be identified as present in a sample, both the retention time and the mass spectra of the peak must match those of the standard.

This SOP requires the use of NIST library spectra to prevent confusion due to co-elution of compounds in the calibration standards; therefore, do not update the target compound spectra in the method.

All ions present in the NIST mass spectra at a relative intensity of 10% of the most abundant ion must be present in the sample spectra.

The relative intensities of the ions must agree within 20% between the continuing calibration verification and sample spectra.

Ions present in the sample at greater than 10% abundance but not present in the standard spectra must be reviewed and accounted for by the analyst making the comparison.

If a compound cannot be verified by these criteria but is present in the technical judgment of the analyst, the supporting evidence must be indicated on the raw data and the analyte reported.

8.1.5.2 Analyte Quantitation

Quantitate the data and print out a quantitation report and chromatogram. Use the average relative response factor from the initial calibration for quantitation.

Review the results as discussed in Section 8.1 for qualitative identification of target analytes. Cross out all reported hits that do not meet the qualitative criteria and delete the compound (Qdel) in ChemStation. Review all target compounds that are detected to verify they are integrated properly. Review the chromatogram for possible false negatives.

Compare the internal standard recovery of the sample against criteria in Appendix C and take corrective action outlined in section 9.4.

8.1.5.3 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow EPA Region 9 Laboratory SOP 835, *Chromatographic Integration*

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Procedures. All manual chromatographic integration must be initialed and dated by the analyst and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.1.6 Calculations

Results for target analytes are calculated using the following equation:

$$(C_x) = (A_x)(C_{is})(DF)/((A_{is})(RRF_{Avg}))$$

Where

C_x	=	Concentration of compound x
A_x	=	Area of quantitation ion of compound x
C_{is}	=	Concentration of the associated internal standard (5 µg/L)
DF	=	Dilution factor
A_{is}	=	Area of quantitation ion for associated internal standard
RRF_{Avg}	=	Analyte average relative response factor from the initial calibration

8.1.7 Review of Tentatively Identified Compound:

The analyst must review the library search results as follows:

- Load the data file of the most concentrated valid analysis of the sample.
- Generate a library search compound (LSC) report; include in the data package.
- Examine the spectra for each peak that is not a target or internal standard.
- Report those TICs for which the response is greater than 20% of the closest internal standard.
- Report a maximum of 10 compounds based on total area (largest).
- Relative intensities of the major ions in the NIST reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum shall be reviewed for possible background contamination or the presence of co-eluting compounds.

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- Ions present in the reference spectrum but not within the scan range of the method should not be considered when making a tentative identification.
- If, in the technical judgment of the analyst, no valid tentative identification of the compound can be made, the compound should be reported as "Unknown 1, 2,…etc.". The analyst shall attempt classification of the unknown compound (i.e., unknown hydrocarbon, unknown aromatic, unknown chlorinated compound, etc.). The probable molecular weight should be included, if distinguishable.

Report the following:

a. Class of compound instead of specific isomers unless the identity of the specific isomer is known. As an example, report dichlorobenzene instead of 1,2-dichlorobenzene. Alternatively, report 1-methylnaphthlene if the calibration standard has 2-methylnaphtalene and the TIC retention time is not that of 2-methylnaphtalene.

b. Report unknowns as Unknown 1, 2 , 3, ….. This ensures that the unknown TICs will be reported correctly by LIMS.

Exclude the following compounds from the report:

a. Analytes eluting prior to the first eluting target compound.
b. TICs that were detected in the method blank.
c. Column bleed (i.e. siloxanes).
d. CO2/fixed gases peaks.
e. Electronic noise peaks.

The concentration of TICs should be estimated. Use the TIC area and assume the RRF is 1.

Use the nearest internal standard free of interferences.

If the base peak saturates the detector, document this in the data. Do not dilute a sample to get the base peak of a TIC within the detector range. If a sample containing a saturated TIC ion was diluted to get a target compound within calibration range, use the TIC area from the diluted analysis to estimate the concentration of the TIC.

Review the chromatogram for a hydrocarbon pattern, generally identified by the presence of a "hump" in the baseline. Place a comment in the LIMS WO memo field if there are fuel hydrocarbons in the sample.

8.1.8 QC Review

As soon as possible after analysis (typically prior to entry into LIMS), inspect sample and QC data for compliance with QC limits in Appendix C. If no significant problems are found, perform the following QC reviews for compliance with SOP requirements:

- Check that target analyte results are within range of the initial calibration.
- Process and review the results for the CCV, QLS, and instrument QC samples. Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV, QLS, and instrument QC results are within QC limits. See Section 9 for instrument QC requirements.
- Process and review the results for the MB, LCS, and MD batch QC samples and verify that the results are within QC limits. See Section 9.3 for batch QC requirements.
- Review all sample results to determine if any samples need to be re-analyzed at a dilution.
- Review the chromatogram for possible false negatives.
- Manually cross out all compounds that do not meet qualitative criteria and document the reason on the quantitation report. Delete the compound (Qdel) in ChemStation.
- If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

8.1.9 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS.

LIMS will report all results to two significant figures and detected results to one-half the QL. LIMs will flag values between one-half the QL and the QL as estimated (J); the analyst must add the C1 flag indicating the result is below the calibration range.

- Generate epatemp.txt files for field and QC samples by printing the report to the screen; these files are used by the LIMS DataTool module to import the instrument results into the Data Entry/Review table.
- Copy sample data files from the local drive to the appropriate instrument

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data subdirectory on the Region 9 LAN to make them available to LIMS and to archive them.

- Create an empty upload file containing the samples analyzed in the LIMS batch or sequence. Import and merge the data files using the LIMS DataTool module. Load the resulting merged data file into the LIMS Data Entry/Review table. See LIMS manual for detailed procedure.

- Edit dilutions in DataTool or LIMS entry table as needed.

- Review results in the LIMS. Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the EPA Region 9 Laboratory Quality Assurance Plan.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook. Routine maintenance procedures and frequency are listed in Appendix H.

8.1.10 Entech Concentrator maintenance

Symptom:

- Decline in chloromethane, bromoform, chloroethane, and/or 1,2-dibromo-3-chloropropane responses or high %RSD for some of the compounds.

  Possible Cause: Trap problem.
  Corrective action: Replace trap if necessary.

- Carryover of high boiling analytes

  Possible causes: Cold spot in system, especially the transfer lines between the autosampler unit and the concentrator or between the concentrator and the GC.
  A sample containing high molecular weight components was analyzed on the system.

  Corrective action: Check temperatures of all heated zones. Adjust temperatures or replace heaters as required. Flush valve, gas lines, and sample lines with methanol or reagent water and bake out.

- Loss of sensitivity to selected analytes and increased pressure to maintain purge flow.

  Possible cause: Degradation of trap.
  Corrective action: Replace trap.

- Loss of all target analytes.

  Possible cause: Leak in system.

  Corrective action: Leak-check autosampler or concentrator system. Inspect quick connects and replace them when worn or distorted.

- Loss of all target or low responses for analytes from a loop coupled with acceptable IS response.

  Possible causes: 1) Low sample canister pressure, 2) Valve misalignment.

  Corrective action:
  1) Check canister pressure and correct problem if one exists.
  2) If canister pressure is acceptable, save the Entech sequence, turn off the power to the Entech autosampler and concentrator, turn the power back on to the autosampler then to the concentrator (must be done in this order). Restart the Entech software.

- Erratic Calibration for all very high and/or all very low boiling analytes coupled with acceptable calibration for other compounds:

  Possible cause: Dirty mass flow controller and/or Pump isolation valves.

  Corrective action: Turn off Entech autosamplers and concentrator power. Remove the right hand side cover of the concentrator (Entech 7100). Locate the Mass Flow Controller (MFC, stainless steel 3"x4"x2" box in the lower front end). The mass flow controller isolation valve is the valve closest to the MFC next to the inside wall (on the left). Carefully remove the clip holding the magnetic coil and remove the coil from the valve. Since the valve screws are easily stripped, care must be taken in removing and reinstalling them. Using an exact fit Philips screw driver, in good condition, carefully remove the 4 screws while firmly applying pressure to the top of screw driver to hold the screw driver in place. Carefully, remove the valve top cover which contains a cylinder and a spring. Sonicate the cylinder and spring in methanol for 1 hour. Carefully clean the inside of the valve with methanol wetted cotton swab. Dry the cylinder and spring at 100°C for 10

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minutes. Reinstall the cylinder, spring, and cover. Reinstall screws by tightening each screw ½ turn each time then moving to the screw across (in the same as installing a car tire) until all screws are tightened. Do not over tighten the screws. Reinstall the magnetic coil. In instances of severe contamination, the Pump Isolation valve (right hand side by the MFC) may have to be cleaned in the same manner. Occasionally, the rubber seal on each end of the cylinder should be reconditioned by applying high viscosity pump oil after cleaning with methanol. Reinstall the concentrator cover. Turn the power back on to the autosampler then to the concentrator (must be done in this order). Restart the Entech software.

8.1.11 GC Maintenance

Symptom

- Carryover

  Possible causes: Analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.

  Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.

  Possible cause: column flow rate problem.

  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and/or smaller peaks.

  Possible causes: column flow rate problem, injection port leak, column butt connector leak, or column contamination.

  Corrective action: As necessary, check for leaks and replace septum. If issues remain, replace the column.

- Loss of resolution.

  Possible causes: column flow rate problem, injection port leak, or column contamination.

  Corrective action: Check for leaks and replace septum. If issues remain, replace the column.

8.1.12 MS maintenance:

Trend to be observed:

- Low m/z 502 to 69 ratio
- Failing tune checks
- Ion 75 in BFB ratio is increasing/failing
  Corrective action: Clean the source.

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory standards as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. The following sections describe quality control measures, criteria, frequency, and corrective action. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in USEPA Region 9 Laboratory SOP 880 *Demonstration of Capability* for more details.

9.2 Instrument QC

9.2.1 GC/MS System Performance Check (BFB analysis):

If the ion abundances fail to meet criteria listed in Appendix C, the BFB chromatogram should be examined for any obvious chromatographic problems. If the problem is determined to be related to poor chromatography, take the necessary corrective action and re-analyze the BFB. If the BFB continues to fail the ion abundance criteria, retune the mass spectrometer. It may be necessary to clean the ion source or take other corrective action to achieve the ion abundance criteria.

If a sample is injected after the time period listed in Appendix C, it must be re-analyzed.

9.2.2 Initial Calibration

Each GC/MS system must be calibrated whenever corrective action is

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performed which may change instrument response (e.g., ion source cleaning, column replacement, etc.) or if the continuing calibration verification acceptance criteria cannot be met.

The data system calculates the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equation.

$$\%RSD = (SD/ RRF_{Avg}) \times 100$$

Where

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (x_i - x_{ave})^2}{n - 1}}$$

The %RSD and SCV recovery requirement is listed in Appendix C.

If an ICAL fails because of one standard, a fresh solution of that standard may be re-analyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that criteria are satisfied before any samples are analyzed.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the EPA Region 9 Laboratory Quality Assurance Plan.

If SCV criteria (see Appendix C) are not met, the SCV must be re-analyzed. If it fails again, prepare a fresh standard. Before continuing with analysis, take corrective action as needed, including reanalysis or re-preparation and reanalysis of the initial calibration if necessary.

9.2.3 Continuing Calibration Verification (may also be evaluated as the LCS)

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard. If the area for any internal standard does not meet the recovery criteria listed in Appendix C, the CCV may be re-analyzed. If the failure is repeated, the analysis shall be terminated, the problem corrected, and a new calibration curve prepared.

Examine retention time of the internal standards in the calibration verification standard. If the retention time for any internal standard does not meet the

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criteria listed in Appendix C, then the chromatographic system must be inspected for malfunctions and corrections must be made, and a new calibration curve prepared.

The data system calculates the percent deviation (%D) of the RF values for each compound using the following equation:

$$\%D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} x\ 100$$

Where:

RRF_C: Relative Response Factor of compound c.
RRF_{avg}: Average Relative Response Factor

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the EPA Region 9 Laboratory Quality Assurance Plan.

If the continuing calibration does not meet %D criteria listed in Appendix C, the analysis shall be terminated, the problem corrected, and a new continuing calibration analyzed.

9.2.4 Quantitation Limit Standard (CRL or QLS)

QLS must be analyzed at the beginning of the analytical run (typically just after the BFB and CCV). The QLS concentrations match the QL concentration (at the instrument). The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

%R	=	percent recovery of the standard.
M	=	measured concentration of the analyte, ug/L.
T	=	true concentration of the analyte in ug/L.

Generate a QLS custom report in ChemStation. Check that recoveries meet criteria specified in Appendix C.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the EPA Region 9 Laboratory Quality Assurance Plan.

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If the QLS recovery does not meet criteria provided in Appendix C, rerun the QLS once to verify. If still unacceptable, determine the cause and take corrective action.

9.3 Batch QC

9.3.1 Method Blank

Analyze method blanks at the frequency listed in Appendix C. MB values ≥½ QL indicate potential laboratory contamination. Use the following guidelines to determine when samples must be re-prepared and re-analyzed:

1. If the MB analyte value ≥½ QL and the sample result is less than five times the MB analyte amount, reanalyze all associated samples containing less than five times the MB analyte amount.
2. If the MB analyte value ≥½ QL and the sample result is greater than five times the MB analyte concentration or is non-detected, report sample result without qualification.

9.3.2 Laboratory Control Sample (equivalent to the CCV in this procedure - one analysis serves both functions)

Analyze LCS at the frequency listed in Appendix C. LCS recovery is calculated as:

$$\%R = \frac{C_m}{C_t} \times 100$$

Where

$\%R$ = percent recovery.
C_m = measured analyte concentration in the LCS.
C_t = true analyte concentration in the LCS.

Generate a LCS custom report in ChemStation. Check that recoveries meet criteria specified in Appendix C.

Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the EPA Region 9 Laboratory Quality Assurance Plan.

If the LCS recovery does not meet criteria provided in Appendix C, rerun the LCS once to verify. If still unacceptable, determine the cause, take corrective action, and re-analyze the LCS and associated samples.

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9.3.3 Matrix Duplicate

Analyze matrix duplicate (MD) at the frequency listed in Appendix C.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmd - C|}{(Cmd + C)/2} \times 100$$

Where

RPD = relative percent difference.
C_{md} = measured concentration in the MD, corrected dilutions.
C = measured concentration in the routine sample, corrected for dilutions.

The RPD limit for all analytes is $\leq$20. If the control limits are exceeded, flag all associated analyte results in the MD source sample as estimated (J).

9.4 Sample QC

9.4.1 Internal Standard Area:

Evaluate the internal standard areas in all field and QC samples immediately after analysis.

The internal standard areas must be within QC limits outlined in Appendix C.

Take the following steps if the internal standard areas are not within the limits:

1. Check the system performance.
2. Re-analyze the sample if a system performance problem is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

If the internal standard areas of the re-analysis are within limits, the problem was within the laboratory's control. Report the results from the re-analysis and submit the data from both analyses. Distinguish between the analysis and re-analysis by adding an "RE" suffix to the sample ID on the re-analysis. The problem must be documented in the LIMS work order memo field.

If the re-analysis does not solve the problem, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis.

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9.5 Method Performance

Appendix I provides a summary of method performance at the 95% confidence level (2σ) based on EPA Region 9 Laboratory data.

Functional areas of the SOP that may be significant sources of analytical error are:

1. Sample degradation. Samples must be stored as outlined in the SOP to minimize losses.
2. Poor column condition may results in inadequate analyte separation and inaccurate integration.
3. Trap condition.
4. Leaks in sample transfer and GC/MS systems.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, SCV, CCV/ LCS, and QLS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

10.2 Analytical sequence

The analytical sequence is documented in the LIMS or in the instrument Run Log. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded. Dilutions are documented in the Dilution Logbook as shown in Appendix G.

10.3 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records. EPA Region 9 Laboratory SOP 845 *Analytical Data Review* provides the typical format for data package deliverables.

10.4 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance.

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- Subsequent instrument modifications and upgrades, including major software upgrades.

- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with USEPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control.*

10.5 SOP Distribution and Acknowledgement

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.6 SOP Revisions

Revisions to this SOP are summarized in Appendix J.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on LotusNotes or the local area network (G:\USER\SHARE\QA PROGRAM\LAB SOPS PDF) for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

Agilent Technologies EnviroQuant ChemStation User's Guide.

Agilent Technologies, Agilent 6890 Series Gas Chromatograph Operating Manuals

Agilent Technologies/HP 5973 GC/MS Users Manual.

Entech Instruments Air Academy Course Manual.

Entech Instruments, Inc.; 7000 Operators Manual; Version 1.1.

EPA Method 0040, *Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar Bags.*

USEPA; Compendium Method TO-14; *Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA7 Passivity Canister Sampling and Gas Chromatographic Analysis. May 1988.*

USEPA; Compendium Method TO-15; *Determination of Volatile Organic Compounds (VOCs) in Soil gas Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)*; January, 1999.

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APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. The applicability of this SOP has been extended to include analysis of samples collected in Tedlar bags.

2. The applicability of this SOP has been extended to cover analytes not listed in method TO-15.

3. Method TO-15 does not explicitly include holding times for samples in canisters. This SOP specifies a holding time of 30 days based on studies referenced in Method TO-15 that indicate stable storage of up to 30 days for most VOCs. The holding time for Tedlar bags is based on information provided in EPA Method 0040, *Sampling of Principal Organic Hazardous Constituents From Combustion Sources Using Tedlar Bags*.

4. This SOP allows for two compounds in the daily calibration to exceed the %D limit of ± 30%. However, the two compounds may not exceed a %D of ± 40%. Method TO-15 does not provide this exception.

5. Method TO-15 specifies 50 ng BFB to be used for checking the instrument tune. This SOP requires a more stringent concentration of approximately 28.6 ng of BFB.

6. Section 2.5 of Method TO-15 describes using the reference spectra generated by the analytical system for target analyte identification. This SOP requires the use of NIST library spectra to prevent confusion due to co-elution of compounds in the calibration standards.

7. This SOP uses LCS QC limits generated from Region 9 Laboratory data. Deviations are allowed for up to 10% of the compounds. Method TO-15 does not make this allowance.

8. Section 10.5.5.2 of Method TO-15 states that the "RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound". This SOP does not address this criterion.

9. Quantitation ion for 2-butanone (MEK) was changed from m/z 43 specified in TO-15 to 72 to eliminate the need for manual integration to separate it from the closely eluting ethyl acetate.

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APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides target compounds and quantitation limits covered by this SOP. Routinely reported analytes are indicated; other listed compounds may be added on a project-specific basis. When required, lower quantitation limits may be reported when supported by method detection limit studies and appropriate QC and calibrations are performed.

ANALYTE	CAS	QL, ppbv	ROUTINELY REPORTED
Propene	115-07-1	1	
Dichlorodifluoromethane	75-71-8	1	
1,2-Dichlorotetrafluoroethane	76-14-2	1	X
Chloromethane	74-87-3	1	X
Vinyl chloride	75-01-4	1	X
1,3-Butadiene	106-99-0	1	
Bromomethane	74-83-9	1	X
Chloroethane	75-00-3	1	X
Bromoethene	593-60-2	1	
1,2-Dibromo-3-chloropropane	96-12-8	1	
Trichlorofluoromethane	75-69-4	1	X
1,2,3-Trichloropropane	96-18-4	1	
1,3-Dichloropropane	142-28-9	1	
2,3-dichloro-1-propene	78-88-6	1	
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	1	X
1,1-Dichloroethene	75-35-4	1	X
Acetone	67-64-1	1	
Carbon disulfide	75-15-0	1	
2-Propanol	67-63-0	1	
Allyl chloride	107-05-1	1	
Dichloromethane	75-09-2	1	X
tert-Butyl methyl ether (MTBE)	1634-04-4	1	
trans-1,2-Dichloroethene	156-60-5	1	
Hexane	110-54-3	1	
1,1-Dichloroethane	75-34-3	1	X
Vinyl acetate	108-05-4	1	
cis-1,2-Dichloroethene	156-59-2	1	X
2-Butanone (MEK)	78-93-3	1	
Ethyl acetate	141-78-6	1	
Tetrahydrofuran	109-99-9	1	
Chloroform	67-66-3	1	X
Cyclohexane	110-82-7	1	
1,1,1-Trichloroethane	71-55-6	1	X
Carbon tetrachloride	56-23-5	1	X
Benzene	71-43-2	1	X
2,2,4-Trimethylpentane	540-84-1	1	
1,2-Dichloroethane	107-06-2	1	X
Heptane	142-82-5	1	

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ANALYTE	CAS	QL, ppbv	ROUTINELY REPORTED
Trichloroethene	79-01-6	1	X
1,2-Dichloropropane	78-87-5	1	X
1,4-Dioxane	123-91-1	1	
Bromodichloromethane	75-27-4	1	
cis-1,3-Dichloropropene	10061-01-5	1	X
4-Methyl-2-pentanone (MIBK)	108-10-1	1	
Toluene	108-88-3	1	X
trans-1,3-Dichloropropene	10061-02-6	1	X
1,1,2-Trichloroethane	79-00-5	1	X
Tetrachloroethene	127-18-4	1	X
2-Hexanone	591-78-6	1	
Chlorodibromomethane	124-48-1	1	
1,2-Dibromoethane (EDB)	106-93-4	1	X
Chlorobenzene	108-90-7	1	X
Ethylbenzene	100-41-4	1	X
m&p-Xylene	106-42-3	2	X
o-Xylene	95-47-6	1	X
Styrene	100-42-5	1	X
Bromoform	75-25-2	1	
1,1,2,2-Tetrachloroethane	79-34-5	1	X
4-Ethyltoluene	622-96-8	1	
1,3,5-Trimethylbenzene	108-67-8	1	X
1,2,4-Trimethylbenzene	95-63-6	1	X
1,3-Dichlorobenzene	541-73-1	1	X
1,4-Dichlorobenzene	106-46-7	1	X
Benzyl chloride	100-44-7	1	
1,2-Dichlorobenzene	95-50-1	1	X
1,2,4-Trichlorobenzene	120-82-1	1	X
Hexachlorobutadiene	87-68-3	1	X
Naphthalene	91-20-3	1	
Bromochloromethane	74-97-5	IS	
1,4-Difluorobenzene	540-36-3	IS	
Chlorobenzene-d5	3114-55-4	IS	

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APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

QC Measure	Criteria	Frequency
BFB	See Table below	Once every 24-hours
IC % RSD[1]	≤ 30%	As needed
CCV %D[1,2]	≤ 30%	One every 24-hours
CCV IS Area	±40% of IC	
CCV IS Retention Time Drift	0.33 minutes (20 sec.) from IC	
LCS Recovery[2,3]	See Table Below	One every 24-hours or 20 field samples
MB	<½ QL	One every 24-hours or 20 field samples
QLS Recovery[3]	60-140%	One every 24-hours or 20 field samples
Matrix Duplicate Precision, RPD[3]	≤ 20%	One per SDG or 20 field samples
Sample IS Area	±40% of CCV	
Sample Retention Time Drift	±0.33 minutes (20 sec.) from CCV	
SCV %D[2]	≤ 30%	One with every initial calibration

(1) Up to 2 compounds may exceed 30% to a limit of 40%.
(2) One injection may be evaluated as both the CCV and LCS.
(3) Up to 10% of the compounds may fail to meet these criteria.

The ion abundance criteria

Mass (m/z)	Relative Ion Abundance Criteria
50	8.0 – 40.0 percent of mass 95
75	30.0 – 66.0 percent of mass 95
95	Base peak, 100 percent relative abundance
96	5.0 – 9.0 percent of mass 95
173	< 2.0 percent of mass 174
174*	50.0 to 120.0 Percent of 95 (Mass 95 must be base peak)
175	4.0 – 9.0 percent of mass 174
176	93.0 to 101.0 percent of mass 174
177	5.0 – 9.0 percent of mass 176

*All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be greater than that of m/z 95.

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Quantitation Ions and Internal Standards

Analyte	IS Reference	Primary Ion, m/z
Propene	1	41
Dichlorodifluoromethane	1	85
1,2-Dichlorotetrafluoroethane	1	85
Chloromethane	1	50
Vinyl chloride	1	62
1,3-Butadiene	1	54
Bromomethane	1	94
Chloroethane	1	64
Bromoethene	1	106
1,2-Dibromo-3-chloropropane	3	157
Trichlorofluoromethane	1	101
1,2,3-Trichloropropane	3	75
1,3-Dichloropropane	3	76
2,3-dichloro-1-propene	2	75
1,1,2-Trichloro-1,2,2-trifluoroethane	1	151
1,1-Dichloroethene	1	61
Acetone	1	43
Carbon disulfide	1	76
2-Propanol	1	45
Allyl chloride	1	41
Dichloromethane	1	49
tert-Butyl methyl ether (MTBE)	1	73
trans-1,2-Dichloroethene	1	61
Hexane	1	57
1,1-Dichloroethane	1	63
Vinyl acetate	1	43
cis-1,2-Dichloroethene	1	61
2-Butanone (MEK)	1	72
Ethyl acetate	1	61
Tetrahydrofuran	1	42
Chloroform	1	83
Cyclohexane	1	56
1,1,1-Trichloroethane	1	97
Carbon tetrachloride	1	117
Benzene	2	78
2,2,4-Trimethylpentane	2	57
1,2-Dichloroethane	2	62
Heptane	2	43
Trichloroethene	2	130
1,2-Dichloropropane	2	63
1,4-Dioxane	2	88
Bromodichloromethane	2	83
cis-1,3-Dichloropropene	2	75
4-Methyl-2-pentanone (MIBK)	2	43

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Analyte	IS Reference	Primary Ion, m/z
Toluene	3	91
trans-1,3-Dichloropropene	3	75
1,1,2-Trichloroethane	3	97
Tetrachloroethene	3	166
2-Hexanone	3	43
Chlorodibromomethane	3	129
1,2-Dibromoethane (EDB)	3	107
Chlorobenzene	3	112
Ethylbenzene	3	91
m&p-Xylene	3	91
o-Xylene	3	91
Styrene	3	104
Bromoform	3	173
1,1,2,2-Tetrachloroethane	3	83
4-Ethyltoluene	3	105
1,3,5-Trimethylbenzene	3	105
1,2,4-Trimethylbenzene	3	105
1,3-Dichlorobenzene	3	146
1,4-Dichlorobenzene	3	146
Benzyl chloride	3	91
1,2-Dichlorobenzene	3	146
1,2,4-Trichlorobenzene	3	180
Hexachlorobutadiene	3	225
Naphthalene	3	128
Bromochloromethane	IS1	49
1,4-Difluorobenzene	IS2	114
Chlorobenzene-d5	IS3	117

LCS and Duplicate QC Criteria (based on laboratory performance at 99% confidence)

Analyte	LCS Recovery, % Lower	LCS Recovery, % Upper	Duplicate Precision, RPD
Propene	72	121	20
Dichlorodifluoromethane	68	129	20
1,2-Dichlorotetrafluoroethane	67	127	20
Chloromethane	70	123	20
Vinyl chloride	69	125	20
1,3-Butadiene	75	121	20
Bromomethane	66	125	20
Chloroethane	67	125	20
Bromoethene	68	124	20
1,2-Dibromo-3-chloropropane	48	162	20
Trichlorofluoromethane	68	133	20
1,2,3-Trichloropropane	61	147	20
1,3-Dichloropropane	64	143	20

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Analyte	LCS Recovery, % Lower	LCS Recovery, % Upper	Duplicate Precision, RPD
2,3-dichloro-1-propene	69	135	20
1,1,2-Trichloro-1,2,2-trifluoroethane	64	125	20
1,1-Dichloroethene	73	128	20
Acetone	67	141	20
Carbon disulfide	45	158	20
2-Propanol	72	132	20
Allyl chloride	75	132	20
Dichloromethane	73	116	20
tert-Butyl methyl ether (MTBE)	74	131	20
trans-1,2-Dichloroethene	80	123	20
Hexane	75	124	20
1,1-Dichloroethane	72	125	20
Vinyl acetate	31	171	20
cis-1,2-Dichloroethene	77	129	20
2-Butanone (MEK)	69	137	20
Ethyl acetate	75	127	20
Tetrahydrofuran	78	120	20
Chloroform	77	126	20
Cyclohexane	76	124	20
1,1,1-Trichloroethane	74	133	20
Carbon tetrachloride	71	141	20
Benzene	81	125	20
2,2,4-Trimethylpentane	82	125	20
1,2-Dichloroethane	61	153	20
Heptane	80	129	20
Trichloroethene	73	128	20
1,2-Dichloropropane	77	129	20
1,4-Dioxane	58	140	20
Bromodichloromethane	76	137	20
cis-1,3-Dichloropropene	80	136	20
4-Methyl-2-pentanone (MIBK)	65	140	20
Toluene	78	133	20
trans-1,3-Dichloropropene	79	146	20
1,1,2-Trichloroethane	74	134	20
Tetrachloroethene	73	130	20
2-Hexanone	50	162	20
Chlorodibromomethane	81	135	20
1,2-Dibromoethane (EDB)	78	133	20
Chlorobenzene	81	126	20
Ethylbenzene	82	130	20
m&p-Xylene	82	131	20
o-Xylene	82	132	20
Styrene	65	141	20
Bromoform	84	137	20
1,1,2,2-Tetrachloroethane	73	127	20

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Analyte	LCS Recovery, % Lower	LCS Recovery, % Upper	Duplicate Precision, RPD
4-Ethyltoluene	81	127	20
1,3,5-Trimethylbenzene	77	132	20
1,2,4-Trimethylbenzene	78	131	20
1,3-Dichlorobenzene	79	124	20
1,4-Dichlorobenzene	75	127	20
Benzyl chloride	67	156	20
1,2-Dichlorobenzene	77	124	20
1,2,4-Trichlorobenzene	55	132	20
Hexachlorobutadiene	52	131	20
Naphthalene	65	135	20

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APPENDIX D.
INSTRUMENT INFORMATION

ENETCH CONCENTRATOR/AUTOSAMPLER MODES OF OPERATION

The Entech concentrator supports three trapping modes, 1) Microscale Purge & Trap (MP&T), 2) Cold Trap Dehydration (CTD), and 3) Focus Only (INJ). Additionally, the concentrator supports two sample introduction modes (Ambient and Loop) within each trapping mode.

A. Microscale Purge & Trap

MP&T eliminates most of the water and CO2 from the sample without loss of the polar and non-polar compounds. MP&T utilizes 3-stages of preconcentration and is normally used for the analysis of most ambient air samples. The series of events are as follows:

1. Sample and standards are preconcentrated on module 1 cryogenically using glass beads
2. Module 1 is warmed to 10°C and slowly flushed with helium to deliver the VOCs to Module 2 while leaving most of the water behind.
3. The sub-ambient Module 2 trap (-30 deg. C) allows the CO2 to pass through it and out to the pump while trapping light to heavy VOCs.
4. The VOCs are thermally desorbed and backflushed off of Module 2 to the focuser (Module 3)
5. The focuser is rapidly heated to inject the sample. The GC is started.
6. Traps 1 and 2 are baked out to prepare for the next analysis.

B. Cold Trap Dehydration

CTD uses trapping temperatures from -10°C to -60°C for both Modules 1 and 2, and is preferred when analyzing samples high in CO2. In this mode, an empty trap is installed in module. The series of events are as follows:

1. Sample and standards are preconcentrated on module 1 & 2 simultaneously.
2. Module 1 is warmed to 10°C and slowly flushed with helium to deliver the VOCs to Module 2 while leaving most of the water behind.
3. The sub-ambient Module 2 trap (-30 deg. C) allows the CO2 to pass through it and out to the pump while trapping light to heavy VOCs.
4. The VOCs are thermally desorbed and back flushed off of Module 2 to the focuser (Module 3)
5. The focuser is rapidly heated to inject the sample. The GC is started.
6. Traps 1 and 2 are baked out to prepare for the next analysis.

C. Focus Only

INJ procedure is used to focus a sample that is at higher concentrations or which was preconcentrated externally. The use of this mode requires prior Technical Director's approval. For the purpose of this SOP, this mode will not be discussed further.

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ENTECH CONCENTRATOR/AUTOSAMPLER METHOD PARAMETERS

Recommended Concentrator operating parameters

The operating parameters for the Entech concentrators. These parameters may vary slightly to optimize instrument responses.

Cold Trap Dehydration(CTD)

CTD Ambient Method:

```
Method Name: C:\Smart\to15.CTD Software ver. 4.20
Report Date/time 10/14/2011 12:03:56 AM

Stream: Sample
 Preflush (sec): 15
 Trap (cc/min): 50
 Volume (cc): 10

Stream: Internal Standard
 Preflush (sec): 5
 Trap (cc/min): 30
 Volume (cc): 40

Stream: Analytical Standard
 Preflush (sec): 5
 Trap (cc/min): 50
 Volume (cc): 0

Stream: Sweep/Purge
 Preflush (sec): 10
 Trap (cc/min): 60
 Volume (cc): 50

Stream: M1 -> M2
 Preflush (sec):
 Trap (cc/min): 5
 Volume (cc): 20


Module1:
 Trap temp(C): -40 Preheat? Yes
 Preheat temp(C): 12
 Desorb temp(C): 12
 Bake temp(C): 150
 Bake time(Min): 7
Bulk1:
 Trap temp(C): 40
 Desorb temp(C): 40
 Bake temp(C): 150

Module2:
 Trap temp(C): -30 Preheat? No
 Preheat temp(C): 50
 Desorb temp(C): 180
 Bake temp(C): 190
```


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```
 Desorb time(C): 3.5
Bulk2:
 Trap temp(C): 40
 Desorb temp(C): 150
 Bake temp(C): 150

Module3:
 Trap temp(C): -160 Focus? Yes
 Inject temp(C): 150
 Inject time(Min):2
 Bake temp(C): 100
 Bake time(Min): 10
 Bake on EventEx# : 3
 Total Time (Min) : 30

Misc:
 Sample Xfer temp(C): 80
 GC Xfer temp(C): 100
 MPOS Valve temp(C): 100
Wait for GC before injecting
Active GC: GC1
 Pressure: 100
 MPOS Valve temp(C): 100
```

CTD Loop Method:

```
Method Name: C:\Smart\LOOP.CTD Software ver. 3.19
Report Date/time 7/11/2011 2:14:05 PM

Stream: Sample
 Preflush (sec): 30
 Trap (cc/min): 10
 Volume (cc): 30

Stream: Internal Standard
 Preflush (sec): 5
 Trap (cc/min): 30
 Volume (cc): 40

Stream: Analytical Standard
 Preflush (sec): 5
 Trap (cc/min): 30
 Volume (cc): 0

Stream: Sweep/Purge
 Preflush (sec): 10
 Trap (cc/min): 60
 Volume (cc): 50

Stream: M1 -> M2
 Preflush (sec):
 Trap (cc/min): 5
 Volume (cc): 20


Module1:
```


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```
 Trap temp(C): -40 Preheat? Yes
 Preheat temp(C): 12
 Desorb temp(C): 12
 Bake temp(C): 150
 Bake time(Min): 7
Bulk1:
 Trap temp(C): 40
 Desorb temp(C): 40
 Bake temp(C): 150

Module2:
 Trap temp(C): -30 Preheat? No
 Preheat temp(C): 50
 Desorb temp(C): 180
 Bake temp(C): 190
 Desorb time(C): 3.5
Bulk2:
 Trap temp(C): 40
 Desorb temp(C): 150
 Bake temp(C): 150

Module3:
 Trap temp(C): -160 Focus? Yes
 Inject temp(C): 150
 Inject time(Min):2
 Bake temp(C): 100
 Bake time(Min): 10
 Bake on EventEx# : 3
 Total Time (Min) : 30

Misc:
 Sample Xfer temp(C): 80
 GC Xfer temp(C): 100
 MPOS Valve temp(C): 100
Wait for GC before injecting
Active GC: GC1
 Pressure: 100
 MPOS Valve temp(C): 100
```


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Entech Loop Split Ratio Setup:

The sample is introduced at a flow rate of 10 mL a minute. The split ratio is determined by the 7032L Split flow. Split flow is set using the following Entech NT 7000 software sequence:

1. From the NT7000 Sequence Table click the View icon
2. Click options on the left hand side of the Microscale Purge and Trap (NT7000) screen.
3. Activate (check on) the 7032L Split Flow option
4. Enter the desired flow in cc/min

The total flow is the sum of 10 cc/minute for the sample the split flow. As an example. Set the split flow to 0 if no split is desired. To attain a 1:2 split, set the Split flow to 10 cc/min. (10 ml sample)/(10 ml sample +10 mL split). Alternatively set the flow rate to 40 cc/min to attain a 1:5 split. Each split level must be stored in a separate method file (i.e. Loop00, Loop10, …). For each sample analyzed, the analyst may specify an ambient or a loop method in the NT7000 Sequence Table. The table below illustrates possible loop split ration/sample size

Loop Method	SPLIT FLOW	SAMPLE SIZE
Loop.CTD	0	1
Loop5.CTD	5	0.67
Loop10.CTD	10	0.5
Loop15.CTD	15	0.4
Loop20.CTD	20	0.33
Loop40.CTD	40	0.2
Loop90.CTD	90	0.1

Refer to the following screen display of a loop method and a typical sequence.

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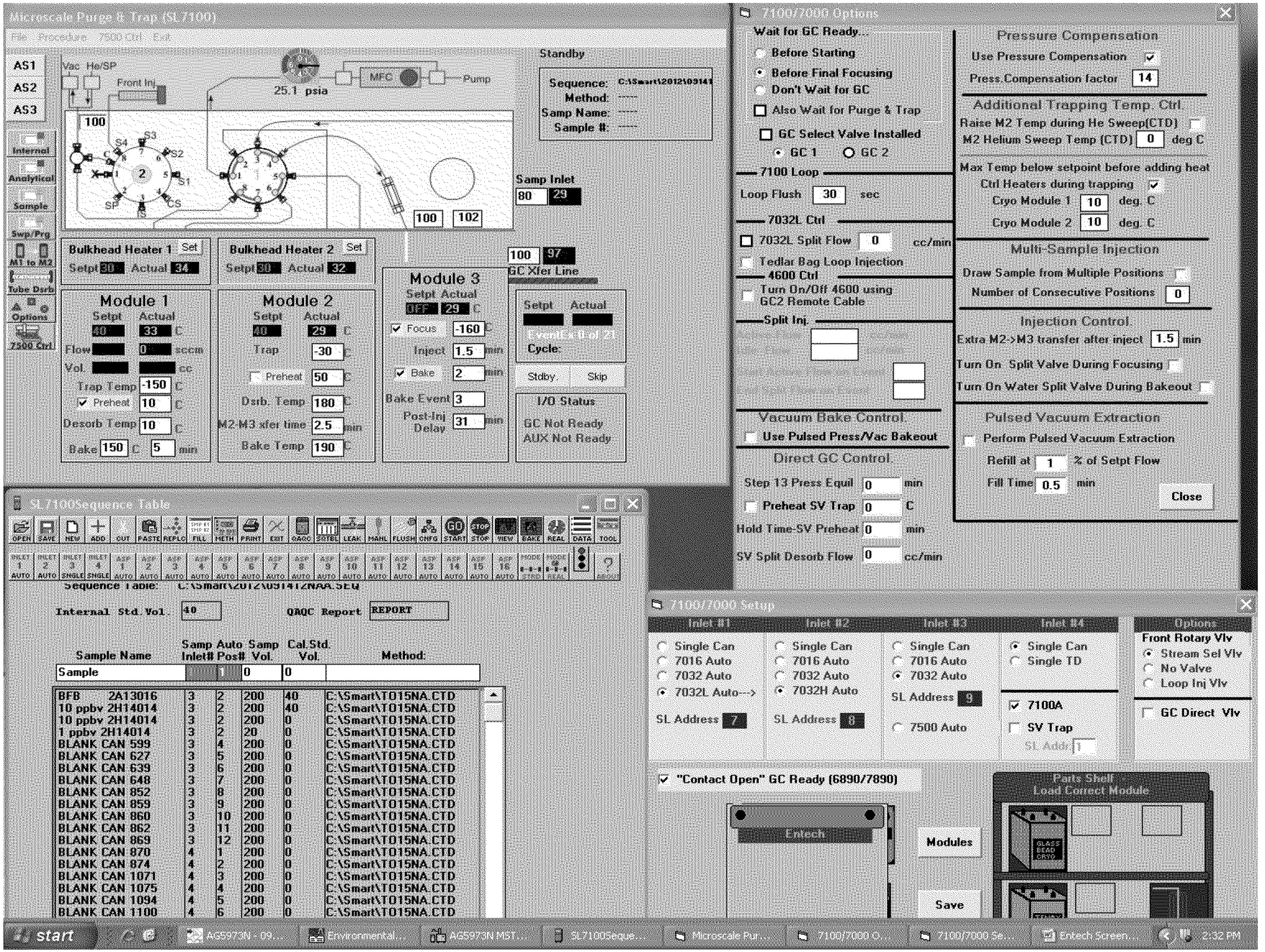
Microscale Purge & Trap (SL7100)
Standby
Sequence:
Method:
Samp Name:
Sample #:
Samp Inlet
Bulkhead Heater 1
Bulkhead Heater 2
Module 1
Module 2
Module 3
GC Xfer Line
7100/7000 Options
Wait for GC Ready...
Before Starting
Before Final Focusing
Don't Wait for GC
Also Wait for Purge & Trap
GC Select Valve Installed
7100 Loop
7032L Ctrl
4600 Ctrl
Split Inj.
Vacuum Bake Control
Use Pulsed Press/Vac Bakeout
Direct GC Control
Pressure Compensation
Use Pressure Compensation
Press.Compensation factor
Additional Trapping Temp. Ctrl.
Multi-Sample Injection
Injection Control
Pulsed Vacuum Extraction
Close
SL7100Sequence Table
Internal Std.Vol.
QAQC Report
Sample Name
Method:
7100/7000 Setup
Inlet #1
Inlet #2
Inlet #3
Inlet #4
Options
"Contact Open" GC Ready (6890/7890)
Entech
Modules
Save
Parts Shelf
Load Correct Module

RECOMMENDED GC/MSD PARAMETERS

HP/Agilent 6890 GC & HP/Agilent 5973MSD

The operating parameters for this system are listed below. Actual operating conditions may vary slightly to optimize instrument

INSTRUMENT CONTROL PARAMETERS

6890 GC METHOD

OVEN

Initial temp:	35 °C (On)	Maximum temp: 255 °C	
Initial time:	7.00 min	Equilibration time: 0.50 min	
Ramps:			
#	Rate	Final temp	Final time
1	10.00	200	0.00
2	12.00	230	0.00
3	20.00	240	3.50
4	0.0	(Off)	
Post temp:	240 °C		
Post time:	6.50 min		
Run time:	30.00 min		

FRONT INLET (SPLIT/SPLITLESS)		BACK INLET (Not used)
Mode:	Split	
Initial temp:	250 °C (On)	
Pressure:	8.42 psi (On)	
Split ratio:	20:1	
Split flow:	30.0 mL/min	
Total flow:	34.3 mL/min	
Gas saver:	On	
Saver flow:	20.0 mL/min	
Saver time:	2.00 min	
Gas type:	Helium	

COLUMN 1 COLUMN 2

Capillary Column (not installed)

Model Number:	RESTEK Rtx 624
	crossbond 6% cyanpropylphenyl 94% dim
Max temperature:	240 °C
Nominal length:	60.0 m
Nominal diameter:	320.00 um
Nominal film thickness:	1.80 um
Mode: constant flow	
Initial flow:	1.5 mL/min
Nominal init pressure:	8.43 psi
Average velocity:	31 cm/sec
Inlet: Front Inlet	

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Outlet: MSD
Outlet pressure: vacuum
FRONT DETECTOR () BACK DETECTOR ()
SIGNAL 1 SIGNAL 2
Data rate: 20 Hz Data rate: 20 Hz
Type: test plot Type: test plot
Save Data: Off Save Data: Off
Zero: 0.0 (Off) Zero: 0.0 (Off)
Range: 0 Range: 0
Fast Peaks: Off Fast Peaks: Off
Attenuation: 0 Attenuation: 0
COLUMN COMP 1 COLUMN COMP 2
(No Detectors Installed) (No Detectors Installed)
THERMAL AUX 2
Use: MSD Transfer Line Heater
Description: MS transfer line
Initial temp: 260 °C (On)
Initial time: 0.00 min
Rate Final temp Final time
1 0.0 (Off)
POST RUN
Post Time: 6.50 min
Oven Temperature: 240 °C
Column 1 Flow: 1.0 mL/min
TIME TABLE
Time Specifier Parameter & Setpoint

7673 Injector

Front Injector:
No parameters specified

Back Injector:
No parameters specified

Column 1 Inventory Number : Varies
Column 2 Inventory Number :

MS ACQUISITION PARAMETERS

General Information
------- -----------
Tune File : Varies
Acquisition Mode : Scan

MS Information
-- -----------

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Solvent Delay : 3.50 min but may vary
EM Absolute : False
EM Offset : Normally 100 V above ATUNE
Resulting EM Voltage : Varies

[Scan Parameters]

Low Mass : 35.0
High Mass : 300.0
Threshold : Varies
Sample # : 3 A/D Samples 8
Plot 2 low mass : Varies
Plot 2 high mass : Varies

[MSZones]

MS Quad : 150 C maximum 200 C
MS Source : 230 C maximum 250 C

END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS

EMISSION : Varies
ENERGY : (70 emv)
REPELLER : Varies
IONFOCUS : Varies
ENTRANCE_LE : Varies
EMVOLTS : Varies
AMUGAIN : Varies
AMUOFFSET : Varies
FILAMENT : Varies
DCPOLARITY : Varies
ENTLENSOFFS : Varies
MASSGAIN : Varies
MASSOFFSET : Varies

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

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Analytical system preparation:

Leak Checking

1. Check that the MSD analyzer temperatures displayed as MS zones are set to the values specified in Appendix D

2. If the display indicates that the analyzer temperatures are not at the desired set points, perform corrective action according to the operator's manual.

3. Check the source analyzer pressure. The analyzer pressure should be less than 10^{-5} torr as indicated by the ion gauge controller. Values higher than indicated above are indicative of large leaks and must be corrected.

4. Check the nitrogen (m/z 28) to water (m/z 18) ratio as follow:

   From View menu in Instrument Control panel of the HP 5973 MSD Instrument, select Perform Diagnostic/Vacuum and then run the Air / Water program from Diagnostics menu. The Air and Water Check report will be printed out. Alternatively, set the mass spectrometer to scan over a range of 10 to 50 m/z. Observe the ratio of the water peak (m/z 18) to the nitrogen peak (m/z 28). If a leak is present in the mass spectrometer the nitrogen peak will be greater than the water peak. Corrective action must be taken if a leak is detected.

Auto Tuning

Perform an autotune of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or the source is cleaned. Perfluorotributylamine (FC43) is the compound used to perform the mass calibration of the instrument. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

Open the HP MSD Instrument Control window and choose the Instrument menu.
Select Perform MS Autotune.

The autotune software will adjust the mass ratio, abundance, peak shape, width, isotope peak resolution, and mass assignment.

An autotune report will be generated and the parameters will be saved in ATUNE.U.

The Agilent ChemStation software requires that the FC43 spectrum meet the following criteria:

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Mass	Target % of Mass 69
50	0.3-5
69	100
131	20-120
219	20-120
414	0.3-10
502	0.3-10

Select Manual Tune from View menu in Instrument Control view and manually tune the MSD, using ATUNE.U as reference. Adjust the parameters of Ion Focus, Entrance Lens, Repeller, Entrance Lens Offset, EM voltage etc to suit your analysis needs.

Save the manual tune file in the format of month-date-year-sequential letter. For example: 082301A.U.

Mass Calibration:

Perform mass calibration of the analytical system at the start of each 24-hour analysis sequence, prior to an initial calibration, whenever the mass spectrometer is shut down, or whenever there is a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer.

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APPENDIX E.
IN-HOUSE STANDARD PREPARATION

Existing VOC standards in methanol may be used to prepare gas phase standards. In preparing the standards, the following issues must be observed:

1. It was previously determined that the largest amount of methanol that may be introduced in the analytical system is 0.5 uL for each analytical run; therefore, it is necessary to minimize the amount of methanol used.
2. To facilitate mixing of the heavy boiling analytes, the can must be quickly pressurized while hot. Analyte condensation and erratic responses may result if the can is allowed to cool prior to re-pressurization.
3. Since most volatile standards are purchased at concentration of 2,000 ug/mL in methanol; intermediate standards must be made to avert having to measure ultra small quantities of standard solution. To reduce the amount of methanol, intermediate standards should be prepared in purged DI water.
4. Prepared standards should be allowed to equilibrate for a period of 24-hours.

Calculate the amount of methanol standard to be used as follow:

$$Vol_x = \frac{Fv * Fc * MW}{IC * 22.4}$$

Where

- Vol_x: Volume of methanol standard in uL.
- Fv: Final volume of prepared gas standard in Liter. For a 6 L cans, Fv is 12, 6L pressurized 2X.
- Fc: Final concentration of gas standard in ppbv.
- MW: Molecular weight of compound in grams/mole
- IC: Initial concentration of methanol standard in ug/mL. Since most volatile standards are purchased at concentration of 2,000 ug/mL, IC = 2000

Prepare an intermediate standard as follow:

1. Pressurize a clean can to 15-16 psia with zero air
2. Open the valve to allow the pressure to return to 1 atmosphere
3. Remove the valve from the can
4. Inject the standard, as calculated above, in the canister at ambient pressure
5. Quickly reconnect the canister valve
6. Tightly cap the canister and place in a 120ºC oven for 1 hour.
7. To facilitate mixing of the heavy boiling analytes, the can is removed from the oven, connected to the diluter, and quickly pressurized to 30 psia while warm
8. The can is allowed to equilibrate back to room temperature
9. The can is re-pressurized to 2X atmosphere to compensate for the drop in pressure due to cooling

The conversion from ppm to ppbv was achieved using the following formula:

$$Fc = \frac{Volx}{Fv\ L\ Air} \frac{IC\ ug}{mL} \frac{1mL}{1000\ uL} \frac{10^{-6}\ g}{1\ ug} \frac{1\ mole}{(MW)\ gx} \frac{22.4\ L\ air}{Mole\ air} \frac{ppb}{10^{-9}}$$

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Example:

The following additional TO15 compounds were required for a project
1,2-Dibromo-3-chloropropane
1,2,3-Trichloropropane

1. 1 ppmv Subset Standard (LIMS ID 9D13007) Used to prepare levels 1, 2, and 5 ppbv via the loop injection:

   The standard was prepared by injecting 7 uL of 2,000 ppm 1,2,3 TCP (LIMS ID 8J29019) and 10 uL of 2000 ppm DBCP (LIMS ID 8J29020) added into 1L can @ ambient pressure. Heated for 1/2 hour @ 99.9 degree C then pressurize up to 29.9 psi while hot. The can was allowed to reach room temperature then re-pressurized to 29.9 psi to compensate for the drop in pressure due to cooling.

2. 20 ppbv Calibration Standard (LIMS ID 9D10020) Used to prepare levels 10, 15, and 20 ppbv via the ambient injection:

   An intermediate standard was prepared by mixing 80 uL of 2,000 ppm 1,2,3 TCP (LIMS ID 8J29019) and 120 uL of 2000 ppm DBCP (LIMS ID 8J29020) into 800 uL of purge and trap grade methanol. The resulting mix was assigned LIMS id 9D09012.

   20 uL aliquot of intermediate standard (LIMS ID 9D09012) was added into 6L can @ ambient pressure. Heated for 1/2 hour @ 99.9 degree C then pressurize up to 29.9 psi while hot. The can was allowed to reach room temperature then re-pressurized to 29.9 psi to compensate for the drop in pressure due to cooling.

   The can was vented in a hood down to ambient pressure (10 uL of original standard remains). The primary standard (LIMS ID 8G16008 @ 100 ml/min, and zero air @ 2400 ml/min) were then introduced in the same can to a final pressure of 29.9 psi.

3. 20 ppbv LCS Standard (LIMS ID 9D13014):

   An intermediate standard was prepared by mixing 200 uL of 200 ppm 1,2,3 TCP (LIMS ID 9C18006) and 25 uL of 2000 ppm EDB/DBCP (LIMS ID 9C18007). The resulting mix was assigned LIMS id 9D10019.

   20 uL aliquot of intermediate standard (LIMS ID 9D10019) was added into 6L can @ ambient pressure. Heated for 1/2 hour @ 99.9 degree C then pressurize up to 29.9 psi while hot. The can was allowed to reach room temperature then re-pressurized to 29.9 psi to compensate for the drop in pressure due to cooling.

   The can was vented in a hood down to ambient pressure. The primary standard (LIMS ID 8J02008 @ 400 ml/min, and zero air @ 600 ml/min) were then introduced in the same can to a final pressure of 29.9 psi.

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The conversion from ppm to ppbv was achieved using the following formula:

$$\frac{20\ uL}{Fv\ L\ Air} \quad \frac{Conc\ x\ ug}{mL} \quad \frac{1mL}{1000\ uL} \quad \frac{10^{-6}\ g}{1\ ug} \quad \frac{1\ mole}{gx\ (MW)} \quad \frac{22.4\ L\ air}{Mole\ air} \quad \frac{ppb}{10^{-9}}$$

Or

$$\frac{448 * Conc\ x\ (ug/mL)}{Fv * (MWx)}$$

Attached is a table of the standards utilized and the final calculated concentration of each target analyte in ppbv.

Compound	MW
1,2-Dibromoethane (EDB)	187.86
1,2,3-Trichloropropane	147.43
1,2-Dibromo-3-chloropropane	236.33

1 ppmv Subset Standard (LIMS ID 9E12013)

Compound	MW	Initial Volume (uL)	Initial Concentration (ug/mL)	Final Volume (L)	Final Concentration (PPBV)
1,2,3-Trichloropropane	147.43	420	200	12	1063.56
1,2-Dibromoethane (EDB)	187.86	60	2000	12	1192.38
1,2-Dibromo-3-chloropropane	236.33	60	2000	12	947.83

Intermediate Standard (LIMS ID 9E12014)

Compound	Initial Volume (uL)	Initial Concentration (ug/mL)	Final Volume (uL)	Final Concentration (ug/mL)
1,2,3-Trichloropropane	80	2000	1000	160.00
1,2-Dibromo-3-chloropropane	120	2000	1000	240.00

20 ppbv Calibration Standard (LIMS ID 9E12016)

Compound	MW	Initial Volume (uL)	Initial Concentration (ug/mL)	Final Volume (L)	Final Concentration (PPBV)
1,2,3-Trichloropropane	147.43	20	160.00	24	20.26
1,2-Dibromo-3-chloropropane	236.33	20	240.00	24	18.96

Intermediate LCS Standard (LIMS ID 9E12015)

Compound	Initial Volume (uL)	Initial Concentration (ug/mL)	Final Volume (uL)	Final Concentration (ug/mL)
1,2,3-Trichloropropane	80	2000	1000	160.00
1,2-Dibromo-3-chloropropane	120	2000	1000	240.00

20 ppbv LCS Standard (LIMS ID 9E12017)

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Compound	MW	Initial Volume (uL)	Initial Concentration (ug/mL)	Final Volume (L)	Final Concentration (PPBV)
1,2,3-Trichloropropane	147.43	20	160.00	24	20.26
1,2-Dibromo-3-chloropropane	236.33	20	240.00	24	18.96

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APPENDIX F.
CHEMSTATION FILE NAMING CONVENTIONS

Files for data, methods, tunes, and sequences on ChemStation computers and the LAN are named using the following naming conventions:

Directories

On the Workstation (When available, use D: drive):

Data:	C:\MSDCHEM \1\DATA\YEAR\DATA\MMDDYYSS or D:\MSDCHEM\YEAR\DATA\MMDDYYSS
Methods:	C:\MSDCHEM\1\DATA\YEAR\METHODS or D:\MSDCHEM\YEAR\METHODS
Sequences:	C:\MSDCHEM\1\DATA\YEAR\SEQUENCE or D:\MSDCHEM\YEAR\SEQUENCE
Tunes:	C:\MSDCHEM\1\5973N or C:\MSDCHEM\1\5975

On the LAN:

Data:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\DATA\MMDDYYSS
Methods:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\METHODS
Sequences:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\SEQUENCE
Tunes:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\TUNE

Methods
MMDDYYATC

Sequence
MMDDYYCSS

Data Files
MMDDYYCSS

Tune Files
MMDDYYA

Variables

A: Enter analysis, as follow:

504	EDB
TO15	TO15
BNA	BNA
BNA (SIM)	PAH or PCP
PEST	PEST
PCB	PCB
RSK175	RSK
TPH-G	GRO
TPH-D	DRO
VOA	VOA

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BFB	BFB
DFTPP	DFT

C: Channel (use when applicable):

Front	A
Back	B
Both	AB

DD: Day i.e. 01, 02, 03, ….

MM: Month i.e. 01, 02, 03, ….

SS: Sequential number 01, 02, 03, ….

T: Matrix Type (if applicable)

Water	W
Solid	S
Air	A
Oil	O
Other	X

YY: Year i.e. 12 for 2012

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APPENDIX G.
DILUTION LOGBOOK, EXAMPLE

AIR/SOIL GAS DILUTION LOG										
DATE / INITIAL	TIME	LAB SAMPLE #	CLIENT SAMPLE #	CAN ID	INITIAL PRESSURE (PSI)	INITIAL VOL (mL)	FINAL VOL (mL)	FINAL PRESSURE (PSI)	AMBIENT PRESSURE (PSI)	DILUTION FACTOR

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APPENDIX H.
PREVENTATIVE MAINTENANCE REQUIREMENTS

GC Maintenance

Item	Frequency	Actions/Comments
Split vent trap	As Needed	Replace.
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Inlet Septum	As Needed	Replace ferrules when changing columns and/or inlet parts.
Column Maintenance	As Needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Replacement	As needed	When trimming and/or solvent rinsing no longer return chromatographic performance.
Ferrules/Column Union	As needed	Replace ferrules when changing columns and/or inlet parts.
Purge/Sample Lines	As needed	Bake out and purge. Clean with organic free water if necessary.
Trap	As needed	Replace when loss of performance.
EM voltage	As needed	If an overall change in sensitivity (area counts in CCV in comparison to most recent ICAL), the EM voltage may need adjusting.

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MS Maintenance

Task	Every Week	Every 6 Months	Every Year	As Needed
Tune the MSD				☐
Check the foreline pump oil level	☐			
Check the calibration vials		☐		
Replace the foreline pump oil		☐		
Clean the ion source				☐
Check the carrier gas traps on the GC				☐
Replace worn out parts				☐
Lubricate sideplate or vent valve O-rings				☐

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APPENDIX I.
METHOD PERFORMANCE

Analysis of Volatile Organic Compounds in Soil Vapor October 24, 2012 – October 24, 2013

Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation (σ)	95% Confidence Interval (2 σ)	
Propene	47	96.2	8.13	79.9	112
Dichlorodifluoromethane	47	98.7	10.3	78.2	119
1,2-Dichlorotetrafluoroethane	47	97.2	9.99	77.2	117
Chloromethane	47	96.2	8.9	78.4	114
Vinyl chloride	47	96.8	9.41	77.9	116
1,3-Butadiene	47	98	7.84	82.3	114
Bromomethane	47	95.7	9.88	76	115
Chloroethane	47	96.1	9.7	76.7	116
Bromoethene	47	95.9	9.44	77.1	115
1,2-Dibromo-3-chloropropane	37	105	19.1	66.7	143
Trichlorofluoromethane	47	101	10.7	79.1	122
1,2,3-Trichloropropane	38	104	14.3	74.9	132
1,3-Dichloropropane	37	103	13.1	77.1	130
2,3-dichloro-1-propene	37	102	11	80.4	124
1,1,2-Trichloro-1,2,2-trifluoroethane	47	94.5	10.2	74.1	115
1,1-Dichloroethene	47	100	9.19	81.7	118
Acetone	47	104	12.4	79.3	129
Carbon disulfide	47	102	18.9	63.9	140
2-Propanol	47	102	9.95	82.2	122
Allyl chloride	47	103	9.48	84.2	122
Dichloromethane	47	94.7	7.24	80.2	109
tert-Butyl methyl ether (MTBE)	47	103	9.5	83.8	122
trans-1,2-Dichloroethene	47	102	7.25	87.1	116
Hexane	47	99.3	8.15	83	116
1,1-Dichloroethane	47	98.3	8.86	80.6	116
Vinyl acetate	47	101	23.4	54.2	148
cis-1,2-Dichloroethene	47	103	8.68	85.4	120
2-Butanone (MEK)	47	103	11.3	80.6	126
Ethyl acetate	47	101	8.68	84	119
Tetrahydrofuran	47	99	6.89	85.3	113
Chloroform	47	101	8.19	84.8	118
Cyclohexane	47	100	8.05	84	116
1,1,1-Trichloroethane	47	104	9.98	83.6	124
Carbon tetrachloride	47	106	11.5	82.9	129
Benzene	47	103	7.42	88	118
2,2,4-Trimethylpentane	47	104	7.15	89.4	118
1,2-Dichloroethane	47	107	15.5	75.9	138
Heptane	47	104	8.02	88.4	121

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Analyte	Number of Measurements	Mean Recovery, %	Standard Deviation (σ)	95% Confidence Interval (2 σ)	
Trichloroethene	47	101	9.14	82.5	119
1,2-Dichloropropane	47	103	8.65	85.6	120
1,4-Dioxane	47	99.2	13.7	71.9	127
Bromodichloromethane	47	107	10.1	86.4	127
cis-1,3-Dichloropropene	47	108	9.32	89.6	127
4-Methyl-2-pentanone (MIBK)	47	102	12.5	77.3	127
Toluene	47	105	9.05	87.3	124
trans-1,3-Dichloropropene	47	112	11.1	90.3	135
1,1,2-Trichloroethane	47	104	9.96	84.3	124
Tetrachloroethene	47	101	9.55	82.3	121
2-Hexanone	47	106	18.7	69	144
Chlorodibromomethane	47	108	8.99	89.8	126
1,2-Dibromoethane (EDB)	47	105	9.28	86.8	124
Chlorobenzene	47	103	7.48	88.2	118
Ethylbenzene	47	106	7.97	90.2	122
m&p-Xylene	47	107	8.19	90.5	123
o-Xylene	47	107	8.28	90.4	123
Styrene	47	103	12.7	77.2	128
Bromoform	48	110	8.87	92.5	128
1,1,2,2-Tetrachloroethane	47	100	9.03	82.3	118
4-Ethyltoluene	47	104	7.65	88.8	119
1,3,5-Trimethylbenzene	47	104	9.32	85.8	123
1,2,4-Trimethylbenzene	47	104	8.82	86.8	122
1,3-Dichlorobenzene	47	102	7.46	86.6	116
1,4-Dichlorobenzene	47	101	8.62	83.7	118
Benzyl chloride	47	112	14.7	82.1	141
1,2-Dichlorobenzene	47	101	7.85	85.2	117
1,2,4-Trichlorobenzene	47	93.4	12.9	67.5	119
Hexachlorobutadiene	47	91.6	13.2	65.2	118
Naphthalene	NA	NA	NA	NA	NA

NA: Not available. Insufficient data points to determine statistics for recently added compounds.

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APPENDIX J
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 311
Revision: 3, Effective: 2/20/2014

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AIR AND SOIL VAPOR

Revision	Effective Date	Description
1	09/14/09	Update limits, include standard preparation, add additional compounds, and minor corrections.
2	04/09/2010	Revised Appendices C and I to reflect laboratory performance from August 2009 to March 2010. Removed requirement to include fuel hydrocarbons in the TIC report.
3	2/20/2014	1. Revised Appendices C and I to current laboratory performance statistics. 2. Changed quantitation ions for 2-butanone (MEK) and ethyl acetate. Added naphthalene as optional analyte. 3. Combined CCV and LCS into one analysis. 4. Minor edits and error corrections throughout the document.

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